

## A square two-dimensional polymer of cobalt citrate cubanes

Larry R. Falvello,<sup>a\*</sup> Elena Forcén-Vázquez,<sup>a</sup> Isabel Mayoral,<sup>b</sup> Milagros Tomás<sup>c</sup> and Fernando Palacio<sup>b</sup>

<sup>a</sup>University of Zaragoza – CSIC, Department of Inorganic Chemistry – ICMA, Pedro Cerbuna 12, 50009 Zaragoza, Spain, <sup>b</sup>University of Zaragoza – CSIC, Instituto de Ciencia de Materiales de Aragón, Pedro Cerbuna 12, 50009 Zaragoza, Spain, and <sup>c</sup>University of Zaragoza – CSIC, Department of Inorganic Chemistry, Instituto de Síntesis Química y Catálisis Homógena (ISQCH), Pedro Cerbuna 12, 50009 Zaragoza, Spain  
Correspondence e-mail: falvello@unizar.es

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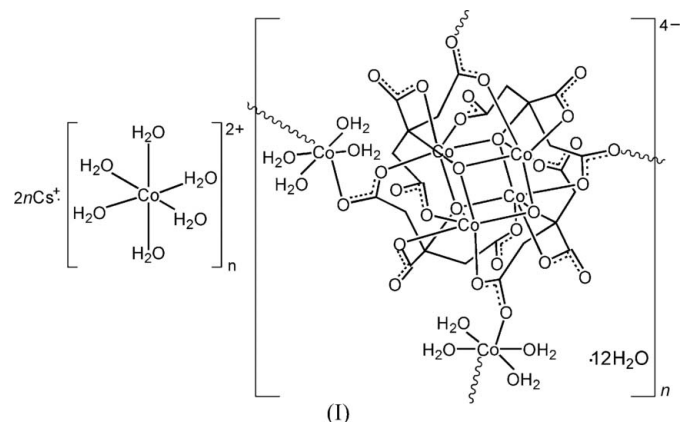
The structure of the title complex, poly[dicaesium(I) hexaaquacobalt(II) [octaaquatetra- $\mu$ -citrato-hexacobalt(II)] dodecahydrate],  $\{Cs_2[Co(H_2O)_6][Co_6(C_6H_4O_7)_4(H_2O)_8] \cdot 12H_2O\}_n$ , at 100 (1) K is formed by layers of a square two-dimensional polymer composed of  $Co^{II}$  citrate cubanes bridged by magnetically active six-coordinate  $Co^{II}$  cations. The polymer has plane symmetry  $p4mm$  in the  $c$ -axis projection. The cubanes reside on sites of crystallographic symmetry  $\bar{4}$ , while the bridging  $Co^{II}$  centres lie on twofold axes. The basic polymeric unit has a charge of  $4-$ , balanced by two  $Cs^+$  and a  $[Co(H_2O)_6]^{2+}$  (symmetry  $\bar{4}$ ) cation, which lie in channels between the polymeric layers. Unligated water molecules, of which there are 12 per cubane, enter into an extended intralayer and layer-bridging hydrogen-bond pattern, which can be described in detail even though not all of the H atoms of the water molecules were located.

## Comment

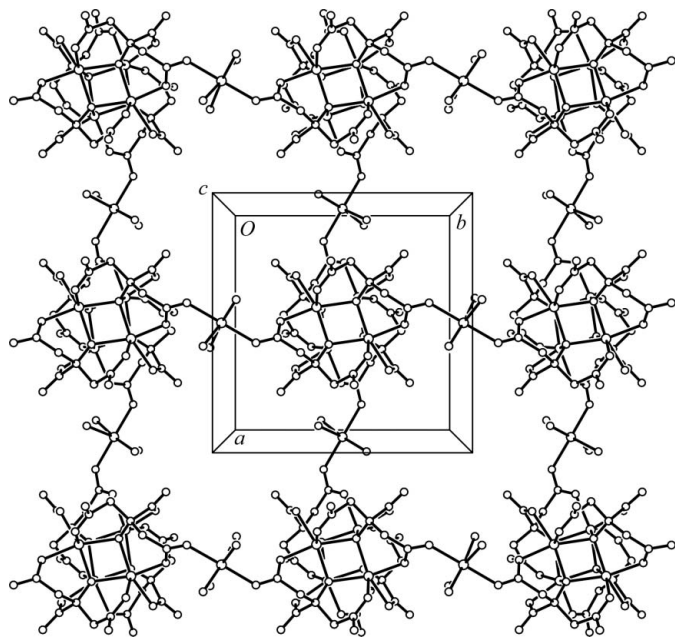
Polynuclear transition metal complexes with cube-shaped cores, generically called cubanes, have been studied for a variety of metals and in a variety of contexts. In recent years, the magnetic properties of cubane complexes of first-row transition elements have been studied, not in small part because the seminal single-molecule magnet (SMM),  $[Mn_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4]$ , has a cubane  $Mn_4O_4$  centre (Lis, 1980; Sessoli, Gatteschi *et al.*, 1993; Sessoli, Tsai *et al.*, 1993). The first cobalt-based SMM (Yang *et al.*, 2002) was a cubane, with deprotonated hydroxymethylpyridine ligands. Murrie *et al.* (2003*a,b*) described a Co-based SMM with citrate ligands. Citrate cubanes of six different transition metals were described by Hudson *et al.* (2006), Moubaraki *et al.* (2008) and Galloway *et al.* (2008). The citrate cubanes in these studies were discrete molecules, either with the basic  $[Co_4(citr)_4]^{8-}$

structure (where *citr* denotes quadruply deprotonated citric acid,  $C_6H_4O_7^{4-}$ ), or with two additional  $Co^{II}$  centres covalently bound at the periphery of the  $[Co_4(citr)_4]^{8-}$  unit to give a tetraanion. We have previously reported a serrated one-dimensional polymer, the structural building block of which is the  $[Co_4(citr)_4]^{8-}$  cubane, and which undergoes an unprecedented reversible crosslinking in the crystal structure to form a rhombic two-dimensional cubane polymer (Campo *et al.*, 2008). In the resulting two-dimensional polymer, a  $Co^{II}$  centre within the crosslinked fragment possesses an uncommon  $CoO_7$  coordination environment. The first three-dimensional network based on the same building block was reported recently (Galloway *et al.*, 2010).

We have now prepared a square anionic two-dimensional polymer, octaaquatetra- $\mu$ -citrato-hexacobalt(II), the structure of which is related to that of a previously reported two-dimensional polymer containing ethylene glycol, (II). The  $Rb^+$  and  $Cs^+$  salts of (II) suffer severe structural disorder but have interesting magnetic properties; these are the subject of another report (Burzurí *et al.*, 2011). In what follows, we report the structure of the title hydrated double salt of this polymer, *viz.*  $\{Cs_2[Co(H_2O)_6][Co_6(C_6H_4O_7)_4][\mu-Co(H_2O)_4]_2 \cdot 12H_2O\}_n$ , (I), which is the first of the square two-dimensional citrate cubane polymers to have crystallized without serious cation and hydrate disorder.



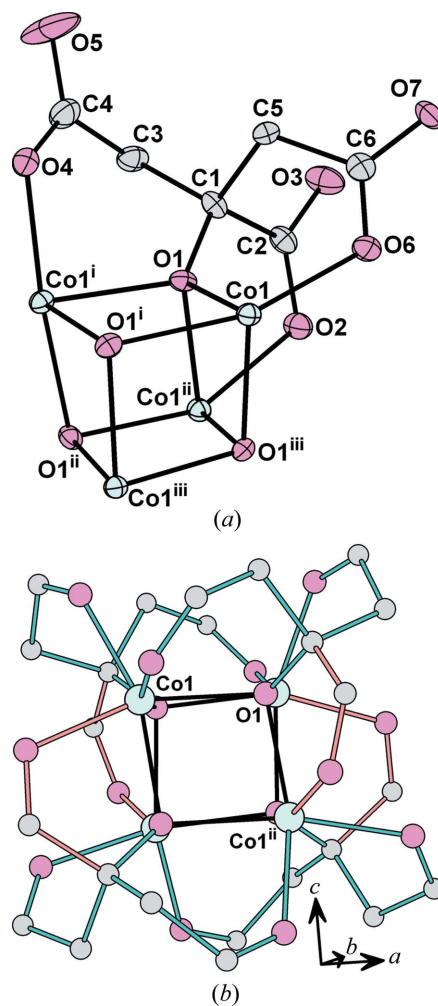
The structure of (I) is a stack of square two-dimensional polymeric layers (Fig. 1). Each layer is a regular array of cubanes located on sites of  $\bar{4}$  symmetry, bridged by six-coordinate  $Co^{II}$  centres which sit on twofold axes. The basic unit of the polymer consists of one cubane and two bridges, *viz.*  $\{[Co_4(citr)_4][\mu-Co(H_2O)_4]_2\}^{4-}$ ; the crystallographic  $a$  and  $b$  axes are the propagation vectors. In chemical terms, it is perhaps better to view the cubane as sharing bridges with each of four neighbours, with the negative charge of one unit of the polymer arising from  $[Co_4(citr)_4]^{8-}$  and one-half of each of the four  $[\mu-Co(H_2O)_4]^{2+}$  bridges, giving a charge of  $4-$  per node of the polymer; there are two nodes per unit cell. Charge is balanced by one  $[Co(H_2O)_6]^{2+}$  and two  $Cs^+$  cations per cubane; these cations are not part of the polymer. The octahedral cation is centred at Co3, which resides on  $\bar{4}$ , giving two per unit cell. Cs1 resides on a set of general positions but is half-occupied, as determined both by the need for charge



**Figure 1**  
The square polymer that forms one layer of the structure of (I).

balance and by the refinement of the displacement parameters to values in line with those of the rest of the structure. There are thus four  $\text{Cs}^+$  cations per cell. One-quarter of the polymer repeat unit, and its associated cations and solvent water molecules, comprise the crystallographic asymmetric unit.

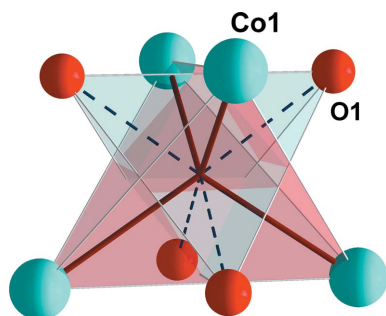
The geometries of cubanes containing Co and Ni have been reviewed by Isele *et al.* (2007). The  $\text{Co}_4\text{O}_4$  core in (I) (Fig. 2 and Table 1) has internal geometry comparable with that observed in previously reported structures based on this unit. The  $\text{Co}\cdots\text{Co}$  and  $\text{O}\cdots\text{O}$  distances are well within the ranges found by Isele *et al.* (2007), and the acute and obtuse bond angles at Co1 and O1, respectively, have commonly observed values that can be related to the magnetic properties of the cubanes. The  $\text{Co}_4\text{O}_4$  fragment in (I) is sufficiently distorted from a regular cubic shape that, for the purposes of describing its geometry, it is best viewed as a stellated octahedron (a distortion of the stella octangula) formed by the interleaved  $\text{Co}_4$  and  $\text{O}_4$  tetrahedra (Fig. 3). The unique  $\text{Cg1}-\text{Co1}$  and  $\text{Cg1}-\text{O1}$  distances are 1.9387 (5) and 1.687 (3) Å, respectively (Cg1 represents the centre of the cubane, located at the unweighted average position of the eight constituent atoms). If the two tetrahedra were considered to be distorted, the  $\text{Co}_4$  unit would be taken as very slightly compressed, with two  $\text{Co}-\text{Cg1}-\text{Co}$  angles greater than, and four less than, the ideal tetrahedral value. The  $\text{O}_4$  tetrahedron might similarly be considered as slightly elongated, although quantitatively the tetrahedral distortion is essentially negligible in both cases, with a Robinson tetrahedral angular variance  $\sigma_{\theta(\text{tet})}^2$  of  $5.72^{\circ 2}$  for  $\text{Co}_4$  and  $2.51^{\circ 2}$  for  $\text{O}_4$  (Robinson *et al.*, 1971). Because of the  $\bar{4}$  symmetry, the quadratic elongation  $\langle\lambda_{\text{tet}}\rangle$  is 1.00. For the purposes of comparison, we have surveyed the geometries of 40 previously published  $\text{Co}_4^{\text{II}}\text{O}_4$  cubane fragments using the Cambridge Structural Database (Version 5.31; Allen, 2002). Structures that we considered to be chemically unrepre-



**Figure 2**  
(a) The core of the cubane unit, which sits on a site of  $\bar{4}$  symmetry. Only the unique citrate ligand is shown. Displacement ellipsoids are drawn at the 50% probability level. (b) The full  $[\text{Co}_4(\text{citrate})_4]^{8-}$  'cubane', showing the five- and six-membered chelates (in the electronic version of the paper, these are in pink and aquamarine, respectively). H atoms have been omitted for clarity. [Symmetry codes: (i)  $-x + 1, -y + 1, z$ ; (ii)  $-y + 1, x, -z + 1$ ; (iii)  $y, -x + 1, -z + 1$ ].

sentative, such as fused cubanes, were excluded from this study. Eight of these published cubane structures displayed a slightly compressed  $\text{Co}_4$  tetrahedron together with a slightly elongated  $\text{O}_4$  unit, and three showed the opposite. None had both tetrahedra elongated. The calculated angular variances  $\sigma_{\theta(\text{tet})}^2$  for the cubanes surveyed varied in the range 0.01–52.9 $^{\circ 2}$  for  $\text{Co}_4$  and 0.05–63.9 $^{\circ 2}$  for  $\text{O}_4$ . In no case did  $\langle\lambda_{\text{tet}}\rangle$  vary by more than 0.02 from the symmetrical value of 1.00 for either of the tetrahedra.

The four citrate ligands of the cubane in (I) are related by  $\bar{4}$  symmetry. Each citrate has its ionized hydroxy O atom as one corner of the cubane. The three terminal carboxylate groups bind through one O atom each to a Co of the cube, thus forming one five- and two six-membered chelates (Figs. 2a and 2b). The five-membered  $\text{Co1}^{\text{II}}/\text{O1}/\text{C1}/\text{C2}/\text{O2}$  ring has an envelope conformation with the fold at  $\text{Co1}^{\text{II}}$  [symmetry code: (ii)  $-y + 1, x, -z + 1$ ]. Numbering from  $\text{Co1}^{\text{II}}$  as the 1 position, this would be rendered as  $E_1$ . The six-membered rings  $\text{Co1}^{\text{I}}$ /

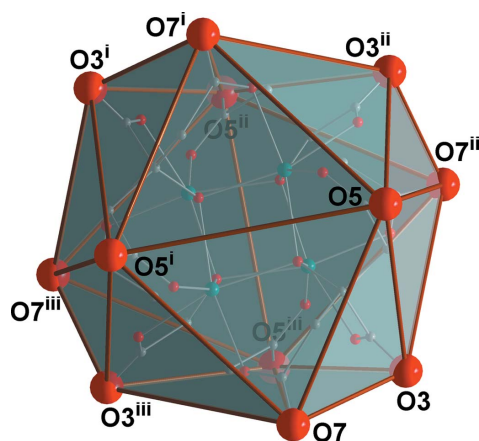


**Figure 3**  
The distorted stellated octahedron composed of interleaved O- and Co-based tetrahedra.

O1/C1/C3/C4/O4 [symmetry code: (i)  $-x + 1, -y + 1, z$ ] and Co1/O1/C1/C5/C6/O6 have ring-puckering parameters (Cremer & Pople, 1975) of  $Q = 0.780$  (3) and  $0.867$  (3) Å,  $\theta = 87.9$  (3) and  $87.8$  (2)°, and  $\varphi = 112.0$  (3) and  $343.7$  (2)°, respectively. Thus, the former has a boat conformation,  ${}^1A$  using the given atom sequence, while the latter is a slightly twisted boat based on  ${}^1A$ .

An important topological feature of the  $[\text{Co}_4(\text{citr})_4]^{8-}$  building block is its periphery, at which 12 partially charged O atoms, namely the carboxylate O atoms not involved in chelation to Co of the cube, offer as many reactive nucleophilic sites, which serve as potential linkage points for forming an ample variety of extended structures in one, two and three dimensions. A number of the citrate cubanes characterized to date have transition metals coordinated by one or more of these peripheral O atoms. The 12 O atoms form an irregular icosahedron (Fig. 4), with  $C_{g1}$ -to-vertex distances of 5.061 (3), 5.428 (3) and 5.535 (3) Å for atoms O3, O5 and O7, respectively. The crystallographic  $\bar{4}$  symmetry relates the vertices in groups of four. Each such group forms a distorted tetrahedron. That formed by atom O5 and its congeners is elongated along  $c$ , with a tetrahedral angular variance of  $889^\circ$ ; this shape, when it appears as a crystal form, is called a tetragonal disphenoid. The tetrahedron containing atom O3 is compressed, with a similar variance of  $828^\circ$ . The O7 tetrahedron is nearly regular, with an angular variance of  $6.7^\circ$ . Atom O7 and its equivalents are the linkage points for the extended structure, binding the 'satellite' atom Co2 and its congeners, which sit on crystallographic twofold axes and bridge successive cubanes. In this way, the cubane/icosahedron and bridging atom Co2 form an unbounded two-dimensional net parallel to the crystallographic  $ab$  plane (Fig. 1). The O7 equivalents from neighbouring cubanes are *trans* to each other at Co2, the coordination of which is completed by four aqua ligands.

Similarities between (I) and previously reported structures with the same cubane building block end at the periphery of the cubane unit. In a previously reported structure of a one-dimensional polymer of Co citrate cubanes (Campo *et al.*, 2008), the analogous icosahedron has similar geometry to that found for (I), with elongated, compressed and regular oxygen tetrahedra having angular variances of 467, 805 and  $38.1^\circ$ , respectively. In that structure, the cubane sits on a general



**Figure 4**  
The icosahedron formed by the peripheral O atoms of four citrate ligands. [Symmetry codes: (i)  $-x + 1, -y + 1, z$ ; (ii)  $-y + 1, x, -z + 1$ ; (iii)  $y, -x + 1, -z + 1$ .]

position and five of its peripheral O atoms bind Co, namely those that are analogous to sites O3, O7, O5<sup>iii</sup>, O3<sup>ii</sup> and O5<sup>i</sup> in Fig. 4. The extended structure in that case does not have the symmetry shown by (I) and the chemical unit formed is a serrated one-dimensional polymer of cubanes. That structure undergoes a chemical reaction in the solid state to form a crosslinked two-dimensional polymer whose icosahedra of peripheral O atoms bind Co at the sites analogous to O3, O7, O5<sup>iii</sup>, O3<sup>ii</sup> and O7<sup>i</sup>, having lost the link to Co at the site analogous to O5<sup>i</sup>.

In (I), the gaps in the polymer mesh of one layer are covered by the cubanes of the two neighbouring layers. The  $\dots ABAB \dots$  stacking of the layers is propagated by  $\frac{1}{2}[111]$ , but alternate layers are actually related by  $n[110]$  and are thus mirror images of each other.

The stacking of the two-dimensional polymeric layers leaves channels in the structure parallel to the  $a$  and  $b$  axes. These are occupied by the  $\text{Cs}^+$  cations (two per polymer repeat unit) along with  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  cations, located on  $\bar{4}$ , and the solvent water molecules.

The hydrogen bonding in (I), although extensive, is not a structure-determining factor; rather, hydrogen bonds are formed within the channels left by the stacking of the anionic polymers, and also between water molecules within the channels and O atoms of the citrate and aqua ligands attached to the Co atoms of the polymer. The seven independent water fragments present (three of them unligated), along with atoms Co2 and Co3 (to which four of the unique water molecules are bound) and their congeners, form a cyclic structure mediated by coordination and hydrogen bonds and which girds the periphery of the icosahedral  $[\text{Co}_4(\text{citr})_4]^{8-}$  unit. The water molecules donate hydrogen bonds to the inner carboxylate O atoms, *i.e.* those that are bound to cubane Co, as well as to the peripheral carboxylate O atoms (Table 2).

This extensive ordered hydrogen-bonding arrangement is not necessary, however, for the stability of the structure. In other systems based on a closely related two-dimensional polymer but crystallized with other cations ( $\text{Rb}^+$ ,  $\text{Cs}^+$  or  $\text{K}^+$ ),

we have observed an isomorphous crystal structure: the two-dimensional layer is stacked in the same arrangement as in (I), but the interlayer space is very different in all cases. Compound (I) is the first case we have observed in which there is no disorder in the non-H atoms of the interstitial residues. In the  $\text{Rb}^+$  and  $\text{Cs}^+$  salts (Burzurí *et al.*, 2011), which are stable in the crystalline state, the cations are disordered over two and three independent sites, respectively, and the interlayer water molecules are severely disordered in the channels. In those structures, the channels account for 39% of the volume of the unit cell, while in (I) 42% of the volume is in the channels. We can speculate that the presence of a larger cation, *i.e.*  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , with its hydrogen-bonding capability, obviates the disordering of the channel contents in (I).

In conclusion, the structure of (I) presents a variety of geometric forms, from the central cubane formed by interleaved tetrahedra to the icosahedron composed of 12 O atoms at the periphery of the basic structural building block, to which are ligated four bridging octahedral  $\text{Co}^{\text{II}}$  centres to form a square two-dimensional polymer. These anionic layers are stacked along the *c* axis, with independent octahedral  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ,  $\text{Cs}^+$  and  $\text{H}_2\text{O}$  in the interlayer spaces. The fact that the interlayer space is ordered in (I) and disordered in two previously reported structures of the same type indicates that the hydrogen-bonding pattern in (I) is not a structure-directing feature.

## Experimental

All reagents were commercially available and were used as received. The title compound, (I), was prepared by adding an aqueous solution of  $\text{CsOH}$  (1.2 M) to an aqueous solution of  $[\{\text{Co}(\text{H}_2\text{O})_4\}[\text{Co}_2(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}]_n$  (Zhou *et al.*, 2005) (0.81 g, 1.00 mmol) until the pH reached 7–8. The resulting mixture was stirred for 30 min and filtered. The addition of 3,3'-sulfanediyldipropyl alcohol (98%) to the solution produced small quantities of pink crystals of (I) with cubic morphology after several months at room temperature.

### Crystal data

$\text{Cs}_2[\text{Co}(\text{H}_2\text{O})_6][\text{Co}_6(\text{C}_6\text{H}_4\text{O}_7)_4 \cdot (\text{H}_2\text{O})_8] \cdot 12\text{H}_2\text{O}$	$V = 3097.11$ (6) $\text{\AA}^3$
$M_r = 1899.11$	$Z = 2$
Tetragonal, $P4_2/c$	Mo $K\alpha$ radiation
$a = 12.5738$ (1) $\text{\AA}$	$\mu = 3.11$ $\text{mm}^{-1}$
$c = 19.5895$ (3) $\text{\AA}$	$T = 100$ K
	$0.16 \times 0.14 \times 0.10$ mm

### Data collection

Oxford Xcalibur Sapphire3 diffractometer	Oxford Diffraction, 2010]
Absorption correction: multi-scan [using spherical harmonics, implemented in SCALE3 <i>ABSPACK</i> scaling algorithm;	$T_{\min} = 0.790$ , $T_{\max} = 1.000$
	14807 measured reflections
	3677 independent reflections
	3128 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.038$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	$\Delta\rho_{\max} = 1.58$ $\text{e \AA}^{-3}$
$wR(F^2) = 0.094$	$\Delta\rho_{\min} = -0.45$ $\text{e \AA}^{-3}$
$S = 1.02$	Absolute structure: Flack (1983),
3677 reflections	with 1567 Friedel pairs
202 parameters	Flack parameter: 0.04 (2)
H-atom parameters constrained	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Co1—O4 <sup>i</sup>	2.037 (3)	O1···O1 <sup>i</sup>	2.719 (5)
Co1—O1	2.087 (3)	O1···O1 <sup>iii</sup>	2.772 (5)
Co1—O1 <sup>iii</sup>	2.090 (3)	O7—Co2	2.078 (3)
Co1—O6	2.096 (3)	Co2—O2W	2.082 (4)
Co1—O2 <sup>iii</sup>	2.124 (3)	Co2—O1W	2.109 (4)
Co1—O1 <sup>i</sup>	2.134 (3)	Co3—O3W	2.078 (3)
Co1···Co1 <sup>i</sup>	3.2252 (11)	Co3—O4W	2.106 (5)
Co1···Co1 <sup>iii</sup>	3.1357 (9)		
O4 <sup>i</sup> —Co1—O1	115.75 (12)	O6—Co1—O2 <sup>iii</sup>	83.95 (12)
O4 <sup>i</sup> —Co1—O1 <sup>iii</sup>	155.97 (11)	O4 <sup>i</sup> —Co1—O1 <sup>i</sup>	86.63 (11)
O1—Co1—O1 <sup>iii</sup>	83.14 (12)	O1—Co1—O1 <sup>i</sup>	80.19 (11)
O4 <sup>i</sup> —Co1—O6	88.35 (11)	O1 <sup>iii</sup> —Co1—O1 <sup>i</sup>	82.01 (11)
O1—Co1—O6	86.86 (11)	O6—Co1—O1 <sup>i</sup>	162.42 (11)
O1 <sup>iii</sup> —Co1—O6	108.35 (11)	O2 <sup>iii</sup> —Co1—O1 <sup>i</sup>	112.64 (11)
O4 <sup>i</sup> —Co1—O2 <sup>iii</sup>	87.66 (12)	Co1—O1—Co1 <sup>ii</sup>	97.31 (11)
O1—Co1—O2 <sup>iii</sup>	154.59 (11)	Co1—O1—Co1 <sup>i</sup>	99.65 (11)
O1 <sup>iii</sup> —Co1—O2 <sup>iii</sup>	77.41 (11)	Co1 <sup>ii</sup> —O1—Co1 <sup>i</sup>	95.87 (11)

Symmetry codes: (i)  $-x + 1, -y + 1, z$ ; (ii)  $-y + 1, x, -z + 1$ ; (iii)  $y, -x + 1, -z + 1$ .

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA···O6	0.95	1.82	2.628 (5)	141
O1W—H1WB···O5W	0.96	1.91	2.829 (5)	160
O2W···O5 <sup>iv</sup>			2.604 (5)	
O2W···O7			2.782 (5)	
O3W—H3WA···O3 <sup>iii</sup>	0.83	1.84	2.662 (4)	168
O3W—H3WB···O5W	0.84	1.98	2.778 (4)	159
O4W—H4WA···O7W <sup>iii</sup>	1.00	1.75	2.736 (5)	167
O5W—H5WA···O6W <sup>vi</sup>	0.91	1.99	2.859 (5)	161
O5W—H5WB···O2 <sup>v</sup>	0.93	1.99	2.905 (5)	167
O6W—H6WA···O7W <sup>iv</sup>	0.85	1.94	2.785 (7)	180
O6W···O2W			2.882 (5)	
O7W—H7WA···O3	0.98	1.83	2.708 (5)	148
O7W—H7WB···O5 <sup>vii</sup>	0.91	1.90	2.749 (6)	153

Symmetry codes: (iii)  $y, -x + 1, -z + 1$ ; (iv)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$ ; (v)  $1 - x, -y, z$ ; (vi)  $\frac{1}{2} - y, \frac{1}{2} - x, -\frac{1}{2} + z$ ; (vii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ .

The Cs1 site was refined with an occupancy of 0.5, which gives charge balance for the structure as a whole and results in displacement parameters of Cs1 in line with those of the rest of the structure. Citrate methylene H atoms were added at calculated positions ( $C-H = 0.99$   $\text{\AA}$ ) and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . For the seven water sites present in the asymmetric unit, of which four are bound to Co, a total of ten H atoms were located in difference maps and included as riding, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . There was no attempt to force or otherwise idealize the O—H distances. Atom O4W is located on a twofold axis and its unique H atom was located. Three H atoms were omitted, namely the two on O2W and one on O6W. The two H atoms attached to O6W were initially placed at positions calculated for donor H atoms in the two interactions in which O6W must be donor. Specifically, O6W must be the donor in hydrogen bonds to O2W [ $D\cdots A = 2.882$  (5)  $\text{\AA}$ ] and O7W<sup>iv</sup> [ $D\cdots A = 2.785$  (7)  $\text{\AA}$ ; symmetry code: (iv)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$ ], because O2W and O7W have two clear hydrogen-bonding contacts each to unprotonated O atoms, and so O2W and O7W<sup>iv</sup> must be the acceptors in their interactions with O6W. Nevertheless, the position of the H atom involved in a putative hydrogen bond from O6W to O2W could not be verified in an omit map, and so this H atom was removed from the model. One H atom attached to O2W, and which is likely the donor in an interaction with O7 [ $D\cdots A = 2.782$  (5)  $\text{\AA}$ ], was neither observed in a difference map nor placed at a calculated position,

because there exists the possibility of minor disorder components in which the second H atom on O2W donates to O1W [2.991 (5) Å] or to O2W<sup>v</sup> [ $D \cdot \cdot A = 2.919$  (8) Å; symmetry code: (v)  $-x + 1, -y, z$ ]. Following refinement, two difference peaks with densities of 1.58 and 1.15 e Å<sup>-3</sup> were found at 0.79 and 1.06 Å, respectively, from Cs1.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, (2007)); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3201). Services for accessing these data are described at the back of the journal.

## References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Version 3. Crystal Impact GbR, Bonn, Germany.
- Burzuri, E., Campo, J., Falvello, L. R., Forcén-Vázquez, E., Luis, F., Mayoral, I., Palacio, F., Sáenz de Pipaón, C. & Tomás, M. (2011). *Chem. Eur. J.* **17**, 2818–2822.
- Campo, J., Falvello, L. R., Mayoral, I., Palacio, F., Soler, T. & Tomás, M. (2008). *J. Am. Chem. Soc.* **130**, 2932–2933.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Galloway, K. W., Schmidtmann, M., Sanchez-Benitez, J., Kamenev, K. V., Wernsdorfer, W. & Murrie, M. (2010). *Dalton Trans.* **39**, 4727–4729.
- Galloway, K. W., Whyte, A. M., Wernsdorfer, W., Sanchez-Benitez, J., Kamenev, K. V., Parkin, A., Peacock, R. D. & Murrie, M. (2008). *Inorg. Chem.* **47**, 7438–7442.
- Hudson, T. A., Berry, K. J., Moubaraki, B., Murray, K. S. & Robson, R. (2006). *Inorg. Chem.* **45**, 3549–3556.
- Isele, K., Gigon, F., Williams, A. F., Bernardinelli, G., Franz, P. & Descurtins, S. (2007). *Dalton Trans.* pp. 332–341.
- Lis, T. (1980). *Acta Cryst.* **B36**, 2042–2046.
- Moubaraki, B., Murray, K. S., Hudson, T. A. & Robson, R. (2008). *Eur. J. Inorg. Chem.* pp. 4525–4529.
- Murrie, M., Teat, S. J., Stoeckli-Evans, H. & Güdel, H. U. (2003a). *Angew. Chem.* **115**, 4801–4804.
- Murrie, M., Teat, S. J., Stoeckli-Evans, H. & Güdel, H. U. (2003b). *Angew. Chem. Int. Ed.* **42**, 4653–4656.
- Oxford Diffraction (2010). *CrysAlis PRO*. Version 1.171.33.55 (release 05-01-2010 CrysAlis171.NET). Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
- Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
- Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.
- Sessoli, R., Gatteschi, D., Caneschi, A. & Novak, M. A. (1993). *Nature (London)*, **365**, 141–143.
- Sessoli, R., Tsai, H. L., Schake, A. R., Wang, S., Vincent, J. B., Folting, K., Gatteschi, D., Christou, G. & Hendrickson, D. N. (1993). *J. Am. Chem. Soc.* **115**, 1804–1816.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Yang, E.-C., Hendrickson, D. N., Wernsdorfer, W., Nakano, M., Zakharov, L. N., Sommer, R. D., Rheingold, A. L., Ledezma-Gairaud, M. & Christou, G. (2002). *J. Appl. Phys.* **91**, 7382–7384.
- Zhou, Z. H., Deng, Y. F. & Wan, H. L. (2005). *Cryst. Growth Des.* **5**, 1109–1117.